Effect of Heat Treatment on Morphology and Dielectric Properties of Polyethylene

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Abstract

Polyethylene is used extensively as an insulating material in high voltage power cables, it is therefore important to understand the behaviour of polyethylene under different conditions. This is a study regarding the relation of heat treatment and the effect of morphological changes on the dielectric properties of polyethylene samples. Polyethylene granulates were pressed to 1 mm thick circular plaque samples that were heat treated differently. The heat treatments were conducted in a vacuum oven. Heat treated samples were tested for morphological changes with Differential Scanning Calorimetry (DSC) and dielectric property changes were studied with an IDAX 300 Dielectric Spectroscopy Analyser and a TREK 30/30 high voltage amplifier, allowing measurements in the frequency range 0.1 mHz – 100 Hz for voltages up to 30 kV. The experimental results were analysed to understand the co-relation among these parameters. A literature review has been conducted on polyethylene morphology to understand their behaviour under different annealing conditions. A phenomenon that has been noticed during the experiments is that the samples swell with annealing; the thickness change effects the dielectric measurements as well. For this reason an extensive study has been conducted on the effect different temperature and time of heat treatment had on the samples.

Heat treatment has effects on the properties of polyethylene samples, but the effect of heat treatment was not only on the morphology but also on the physical dimension of the samples. The samples change their thickness with heat treatment along with their morphology. The effect of morphological changes on the dielectric property of polyethylene samples has not been found to be eminent.

This study was focused on relatively thicker samples (1 mm) compared to the existent scientific literature (0.1-0.2 mm). There are very limited research literatures available on the relation of morphology and electrical properties of polyethylene; this work is an attempt to contribute to the knowledge. Also the effect of samples swelling with annealing and its effect on electric measurements is not found in existing literatures. This work will also contribute understanding the effect of sample swelling on measurements.

Key words: Polyethylene, Morphology, Annealing, Sample Swelling, Dielectric Spectroscopy, Differential Scanning Calorimetry, Crystallinity, heat Treatment, Power Cable, High Voltage, Permittivity
Sammanfattning

Polyeten används i stor utsträckning som ett isolermaterial i högspänningskablar, och därför är det därför viktigt att förstå beteendet hos polyeten under olika förhållanden. Detta är en studie angående relationen mellan värmebehandling och effekten av morfologiska förändringar av de dielektriska egenskaperna hos polyeten. Polyeten granulat pressades till 1 mm tjocka cirkulära skivor som sedan värmebehandlades olika. Värmebehandlingarna utfördes i en vakuumugn. De värmebehandlade proverna testades för morfologiska förändringar med differentiell svepkalorimetri (DSC) och dielektriska egenskaperna studerades med en IDAX 300 Dielektrisk spektroskopi Analysator och en TREK 30/30 högspänningsförstärkare, vilken tillåter mätningar i frekvensområdet 0,1 mHz - 100 Hz för spännings upp till 30 kV. De experimentella resultaten analyserades för att förstå relationen mellan dessa parametrar. En litteratur har utförts på polyeten morfologi för att förstå deras beteende under olika anlöpningsförhållanden. Ett fenomen som har uppmärksammat under experimenten är att proverna sväller med anlöpningen. Även tjockleken påverkar de dielektriska mätningarna. Av denna anledning utfördes en omfattande studie av effekten av olika temperatur och tid för värmebehandling hade på proverna.

Värmebehandling har effekter på egenskaperna för polyetenprover, men effekten av värmebehandlingen var inte bara på morfologin, utan också på den fysiska dimensionen av proverna. Effekten av morfologiska förändringar på den dielektriska egenskapen hos polyetenprover har inte befunnits vara framstående.

Denna studie var inriktad på relativt tjockare prover (1 mm) jämfört med den existerande vetenskapliga litteraturen (0,1-0,2 mm). Det finns mycket lite litteratur kring relationen mellan morfologi och elektriska egenskaper hos polyeten; detta arbete är ett försök att bidra till kunskapen. Även effekten av provernas svällande efter anlöpning och dess effekt på dielektriska mätningar finns befintliga litteraturen.

Nyckelord: Polyeten, Morfologi, Anlöpning, Svällning, Dielektrisk spektroskopi, Differentiell svepkalorimetri, Kristallinitet, Värmebehandling, Kraftkabel, Högspänning, Permittivitet
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List of Symbols

$S$: Complex power [VA]
$P$: Real power [W]
$U$: Voltage [V]
$I$: Current [A]
$R$: Resistance [Ω]
$M$: Molar mass [g/mol]
$\varepsilon$: Permittivity [F/m]
$\varepsilon'$: Real permittivity [F/m]
$\varepsilon''$: Imaginary permittivity [F/m]
$tan\delta$: Dissipation factor
$D$: Displacement field [C/m²]
$E$: Electric field [V/m]
$P$: Polarization
$\chi(\omega)$: Susceptibility
$C'$: Geometric Capacitance [F]
$C''$: Imaginary capacitance [F]
$i_r$: Loss current [A]
$i_c$: Capacitive current [A]
$\delta$: Dielectric loss angle [°]
$W_c$: Crystallinity
$\Delta h_{exp}$: Enthalpy of the test sample [J/g]
$T_m$: Desired temperature to calculate crystallinity [K]
$T_1$: Lower limit of integration to calculate crystallinity [K]
$\Delta h_f$: Heat of fusion [J/g]
$C_{pa}$: Heat capacity of amorphous PE [J/K]
$C_{pc}$: Heat capacity of crystalline PE [J/K]
$\sigma_{dc}$: Conductivity [S/m]
i: Imaginary unit [K]
$T_{melt}$: Melting temperature [K]
$T_m^*$: Equilibrium melting temperature [J/m²]
$\sigma_f$: Surface free energy [K]
$L$: Lamellar thickness [Å]
$\varepsilon_s$: Low frequency static permittivity [F/m]
$\tau$: geometrical impedance
$L$: Thickness of crystals [Å]
w: Width of crystals [Å]
List of Acronyms

PD: Partial Discharge
HVDC: High Voltage Direct Current
AC: Alternating Current
HVC: High Voltage Cable
PE: PolyEthylene
DSC: Differential Scanning Calorimetry
DS: Dielectric Spectroscopy
HDPE: High Density Polyethylene
LDPE: Low Density Polyethylene
PET: PolyEthylene Terephthalate
PTFE: PolyTetraFluoroEthylene
MI: Mass Impregnated
XLPE: Cross Linked Polyethylene
HVU: High Voltage Unit
DFT: Discrete Fourier Transform
HDT: Heat Distortion Temperature
Chapter 1

1. Introduction

1.1. High Voltage Power Cables

Power cables are used to transmit electricity from the generating units to the end users. Electric power cables come in different size and shapes but the basic structure of the cable remains the same; it is an established design consisting of a conducting material to carry the current and a protective insulating sheath to cover the conductor. Other layers are added with this basic structure depending on the application of the cables. In the last century lots of researches has been performed in the development of power cables to increase the power transfer ability, reliability and longevity. The power transfer ability of the cables mainly depends on the voltage level and current level, and can be expressed in a simplistic way by this formula in general,

\[ S = U \cdot I \]  \hspace{1cm} 1.1

Any of these two values can be increased to increase the transferred power, but increasing the current also increases the loss in the transmission system due to resistive loss,

\[ P_{loss} = I^2 \cdot R \]  \hspace{1cm} 1.2

Higher current will also require a larger conductor. For these reasons, generally when required to go to a higher level of power transfer the voltage is increased instead of the current. When the voltage is increased less current is required for a specific power level and a smaller conductor can be used, but higher voltages require a better insulation for the cable. This is why in the past decades many of the cable related researches have been done on improving different types of cable insulation.

Since electricity is mostly generated as alternating current (AC) it is also mostly transmitted to the consumers as AC, even though AC transmission has had some limitations, such as transmission capacity, distance constraints and connecting different asynchronous AC networks of different voltages. But with the expansion of power systems the need for long distance power transmission is increasing day by day. HVDC power transmission is better for long distance and higher power transfer than AC transmission economically, so in recent years there has been a re-emergence of HVDC transmission due to better economical, technical and environmental advantages. With HVDC two asynchronous grids can be connected and the power flow can be controlled better; it also has lower short circuit current, reduced requirement on right of way and lower investment cost for long distances [1].
In this thesis the focus is on HVDC cables, hence power cables and HVDC cable will be used interchangeably. For high voltage DC cables there are two types of insulations used, mass impregnated and polymeric insulations. Since 1950s, HVDC mass impregnated (MI) cables have been used in large submarine power transmission projects at the highest DC voltage levels. MI cables are rated up to 600 kV DC. The very first HVDC cable introduced by ABB in 1954 connected between the island of Gotland and mainland of Sweden in the Baltic Sea was also a MI cable [2].

![Figure 1.1: ABB HVDC MI cable [3]](image)

In the mid-1990s, ABB developed, produced and installed a complete high-voltage direct current (HVDC) extruded cable system. In extruded cables the insulation is generally some cross linked polymer, mainly polyethylene. The ABB extruded cable system is also known as HVDC light, it offers reduced weight and size of the cable and more power transfer per kilogram of cables. The new world record of voltage level for extruded cable is 525 kV [4] was set by ABB recently.

![Figure 1.2 : ABB HVDC extruded cable [4]](image)
MI cables are relatively costly and due to the use of oil are also environmental concerns, so the extruded cables are now thought to be the future of power transmission. Research is being conducted to increase the voltage levels of the extruded cables by improving the insulation of the cables. The insulation used in HVDC extruded cable is mainly XLPE, which is cross-linked polyethylene. Thus to improve the voltage level of XLPE cables it is important to increase the knowledge of how polyethylene behaves under different conditions to understand and improve the manufacturing and operational process.

Heat treatment helps to improve the electrical properties of extruded DC cables. Heat treatment affects the electrical properties of polymers via two main phenomena; first, heat increases the speed with which mobile polar substances diffuse out of the system. The polymers used in cable insulation are mainly consist of non-polar carbon-carbon and carbon-hydrogen but small amount of residue catalyst, humidity or other polar molecules can increase the conductivity. The diffusivity of the polymer can be expressed as a function of amorphous content, geometric impedance and chain immobilization factor [5].

Strictly geometric impedance ($\tau$) can be a complex function of crystalline content as well of crystallite size, shape and orientation [6]. The morphology of semi crystalline material can be related to the geometric impedance by using the modified Fricke model [6] [7]. Geometric impedance ($\tau$) is related to Crystallinity ($W_C$), lamellar thickness ($L$) and width of crystals ($w$). The morphological parameters in a material are influenced by the heat treatments and thus influence the diffusivity of the molecules from PE.

Secondly, heat has an annealing effect on the polymer in which by increasing the polymer chains degrees of freedom of movement allows for faster relaxation of the polymer chains and creation of crystallites. When annealed to a temperature above the temperature of the crystal formation and below the melting point, single crystals change their appearance. They do not melt but retain their shape and seem to get thicker [8]. During isothermal crystallization the crystallinity increases with time, and when a little less than half of the final crystallinity is reached the rate slows down [8]. According to the theory the crystallite thickening rate rapidly increases with temperature and $1/M$ in PE [9], where $M$ is the molar mass of the sample.

Any changes in the polymer structure by heat treatment may lead to change in energy, density and distribution of trap levels resulting in the change of its DC conductivity [10]. The influence of several parameters (field, temperature, humidity) on conduction current can be found in literature but however the influence of structural changes of PE under temperature and subsequent dielectric property changes is not very well studied. This thesis focuses on dielectric and morphological characteristics of polyethylene as insulating material and understanding its behaviour under certain temperature conditions.
1.2. Aim and Objectives

1.2.1. Aim

The aim of this thesis is to study the relation between morphological changes and the dielectric properties of polyethylene caused by thermal treatment.

1.2.2. Objectives

The main objectives of this thesis are,

- To evaluate the effect of morphological changes of thermal annealing on dielectric properties of polyethylene by experiments on thick plaque samples of 1 mm.
- To characterize and evaluate the effect of thermal annealing on the morphology of polyethylene.
- To study the correlation between morphology of polyethylene and its dielectric properties.

Three factors are to be considered in this work, and the correlation between them is to be determined for polyethylene samples,

- Heat treatment
- Morphology
- Dielectric property

The goal of this thesis is to evaluate the relation between morphology and dielectric properties of polyethylene via annealing effects and morphological changes.

1.2.3. Method

PE sample will be heat treated and that will affect their morphology, the morphological change will result in changes in electrical properties. If a specific sample is heat treated and later tested for morphological and dielectric property changes due to heat treatment, one can find out the relation among them. If a series of experiments are conducted it would be possible to see the direction and interdependency of the correlations between these factors.

1.3. Main Results

Heat treatment has effects on the properties of PE samples, but surprisingly the effect of heat treatment was not only on the morphology but also the physical dimension of the samples. The samples change their thickness with heat treatment along with their morphology. When measuring the samples one needs to correct the results for thickness change to see the effect of morphological changes. The effect of morphological changes on the dielectric response of PE samples has not been found to be very strong, at least down to the frequency $10^3$ Hz;
small changes are seen at lower frequencies as it enters the conduction region. But again spectroscopy is not the best tool to measure the conduction change in samples. The results and details discussion is added in the later chapters of the report.

1.4. Thesis Disposition

The report has been written in a way so that anyone with minimum background on the topic can read and understand the basic concept of the work and the outcome of the thesis. Small notes on very basic of power transfer, HVDC, cable insulation and measurement technique for different parameters has been added in the report in the first chapter. The second chapter consists of theories on different topics of the thesis and mainly important for someone with electrical engineering background to understand a little about PE as a material. The third chapter lists the equipment used for the work and their basic description, also an outline on how different equipment was used in this work and their tuning and calibration. The fourth chapter describes the methodology of the work and how it was developed, the different factors in consideration and how they were taken into account along with the final results for the thesis, small comments on them were added and they were discussed in details in chapter five. Chapter six is about concluding remarks on the work and its future prospect. Additional supporting documentations are included in the appendix of the thesis.
Chapter 2

2. Theory

In this chapter the basic theories related to polyethylene morphology, different properties of polyethylene and complex permittivity are presented briefly.

2.1. Polyethylene

Cross-linked polyethylene (XLPE) is a form of polyethylene which is manufactured by using cross linking agents to create cross linking among the polymer chains. Generally there are two types of PE classified according to their molecular weight as HDPE and LDPE, but for high voltage cable insulation LDPE is used mainly. HDPE has a higher melting point and higher crystallinity. However, this makes the material stiffer (higher modulus, etc.). LDPE has lower melting point and lower degree of crystallinity, but is then more flexible. In order to increase the thermal stability the material is cross-linked using peroxides. The cross-linked polyethylene is flexible and maintains its shape at higher temperatures thanks to the cross-linked structure [11]. LDPE is mostly used as HV cable insulation. In this thesis LDPE samples supplied by ABB HVC were tested.

2.1.1. Morphology

The significant property of PE is its semi crystalline morphology that means there are two or more components that make the structure of the polymer; the material is a mixture of the two or more components. As one of the components consist of molecular chains are structured in a three dimensional array and in one and more phases chains are disordered [12]. The non-crystalline part forms a matrix in which the crystalline regions are embedded. The amount of crystalline and non-crystalline part in a specific material governs the properties of that material; the different types of commercial PE are manufactured mainly by changing the ratio of crystalline and semi-crystalline parts to achieve the specific need for that application. Completely crystalline PE would be very friable and completely non-crystalline PE would be fluidly, so a mixture of both makes usable PE.

The structure of PE can be divided into three regions [12]:

- Crystallites
- Non Crystalline
- Interfacial Region

High density PE crystallites are commonly 80-200 Å thick with lateral dimension up to few micrometers and for low density PE they are smaller. The non-crystalline regions separating the crystallites can be 50-300 Å [12]. Interfacial regions are difficult to characterize. In much
literature ‘amorphous’ is used to describe the non-crystalline region as a whole but at times this can be misleading, because it contains both disordered and partially ordered regions. In this study the main focus is into the amount of crystallinity so this would not be a major concern. In this report the term ‘amorphous’ is therefore used commonly for any non-crystalline region of the material. The amount of crystallinity can be measured by different methods but in this work Differential Scanning Calorimetry (DSC) is employed to study crystallinity and the structure of PE samples.

Figure 2.1: 3D model of partially crystalline PE [13]

PE is one of the most common polymers used and it has been used as semi crystalline polymer for morphological studies because of its simple chemical structure [6]. There are three phases of PE, i.e. the melt, orthorhombic and hexagonal; the orthorhombic is the most stable phase under ambient temperature and pressure [6]. The hexagonal phase is only found in mechanically stressed samples [14]. The three phases of PE coincide at one point in pressure – temperature diagram, this triple point occurs at 250 °C and 0.33 GPa [15].

When PE crystallizes from melt the chains are organized by folding to form lamellae [6] and it is observed that the crystal shape of PE changes with time between the crystallization temperature and the final melting point [16]. The higher the degree of crystallinity the better the organization of lamellae within it; lamellae and crystallites are used interchangeably in PE morphology [12]. Except for the obvious molecular structural factors, the thickness of the crystal lamellae is dependent on the crystallization condition, which is mainly the crystallization temperature, pressure, shear and other annealing treatments [17]. Well-formed
and thick crystals are formed when the PE is crystallized at a low level of supercooling i.e. high crystallization temperature. And short, thin and curved crystals are formed when PE is crystallized at a higher level of supercooling i.e. lower crystallization temperature [18]. The crystallization process does not stop when the sample is cooled down to room temperature; secondary crystallization may occur at a slower rate at room temperature, which can make the material more dense and tighten the packing [12]. The degree of crystallinity is unlikely to increase more than 2-3 percent by secondary crystallization [12].

When PE is crystallized from melt depending on the molar mass and temperature it can form different kinds of superstructures. Axialites were formed at the highest temperatures, non-banded spherulites at intermediate temperatures, and banded spherulites at the lowest temperatures [19]. Low molar mass PE (M<17000 g /mol) forms superstructures at all crystallization temperatures [20] and very high molar mass PE crystallizes without any clear superstructure at all temperatures [21]. By controlling the cooling temperature and also by annealing, one can control the amount of crystallization and superstructure in a specific sample and thus controlling their solid state properties. This thesis is an attempt to contribute to the scientific ability to predict the physical properties of a PE resin based on its molecular structure.

2.1.2. Electrical Properties of PE

Polyethylene is a very good insulating material; there are no free electrons, polar bonds and therefore it is inert to electric field and that is why it is extensively used in high voltage power cables. Under high electric field trace of polar molecules (catalyst residues, water, and polarizable bonds) can contribute to increased conductivity. Under high electrical stress PE deteriorates both chemically and physically [12]. There are generally a few electrical properties characterizing in an insulating material,

- Resistivity
- Permittivity
- Dissipation factor
- Dielectric strength
- Arc resistance
- Treeing resistance

The bulk resistivity of PE does not only depend on the chemical structure but also on added antioxidants, catalyst residues and water or other polar molecules. In pure PE these are present in very small amounts and affect the resistivity. Bulk resistivity is also affected by temperature and to a much lesser extent by humidity, pressure and morphology of that particular sample [12]. Volume resistivity of LDPE and HDPE is in the scale of $10^{-16}$ Ωm [22].
When the voltage applied across an insulator is increased there comes a point at which the electrical resistance breaks down. The voltage at which such breakdown occurs is known as the dielectric strength of the insulator. Dielectric strength varies with thickness, temperature, humidity etc. of the sample [12]. It is also time dependent, the paths along which current can flow takes time to develop. Increased crystallinity and spherulites diameter increases dielectric strength while higher temperature and humidity decreases the dielectric strength [23]. Dielectric strength is also time dependent, the continued exposure to an electric field tend to decrease the dielectric strength of PE due to the growth of conductive paths, time to failure decreases at higher temperature and humidity [24]. An increase in temperature decreases the dielectric strength because at elevated temperature the crystallites start to melt [12]. That is why polyethylene insulated cables usually have a maximum operating temperature.

Arc resistance of a material is the time its surface can be exposed to an electric arc before it breaks down and conducts current. Arc resistance of PE varies widely in the literature. For LDPE the arc resistance is in the range of 135-160 seconds [12].

PE insulation fails under high field stress by formation of conductive paths known as ‘trees’, the name comes from the pattern of the paths.

Trees occur due to voids, contaminants, notches or protrusions working as electrical stress concentrators. Increasing an electrical stress generally causes acceleration in the growth rate of trees [26]. Elevated temperatures increase the growth rate of trees in most cases [25].

### 2.1.3. Thermal Properties of PE

As a semi crystalline material PE differs from the crystalline solids. PE displays a melting range rather than a discrete melting point. It undergoes a transition from the semi crystalline to the molten state that takes place over a range that can span from 10 °C to 70 °C [12]. The peak melting temperature of LDPE ranges from 105-115 °C [12]. The effect of molecular,
processing and morphological characteristics on peak melting temperature are given in the Table 2-1.

Table 2-1: Effect of different variables on melting temperature

<table>
<thead>
<tr>
<th>Variable</th>
<th>Effect on Melting temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increased branch content</td>
<td>Decrease</td>
</tr>
<tr>
<td>Increased molecular weight</td>
<td>Decrease</td>
</tr>
<tr>
<td>Decreased crystallinity</td>
<td>Decrease</td>
</tr>
<tr>
<td>Increased cooling rate</td>
<td>Decrease</td>
</tr>
<tr>
<td>Increased Orientation</td>
<td>Increase</td>
</tr>
</tbody>
</table>

Heat distortion temperature (HDT) is the temperature at which polymers begins to show appreciable deformation, it can be used as a guide to its maximum service temperature. HDT of PE is also related to the crystallinity. Thermal expansion of PE depends on two factors, the relative proportion of ordered and disordered regions and the orientation of the crystallite axis with respect to the direction in which the expansion is being measured. Disordered regions exhibit higher expansion due to the inherently higher degree of freedom of movement. Naturally the expansivity of a sample increases with temperature as a greater proportion of sample is converted from ordered to disordered phase [12]. In the following Figure 2.3 thickness change for samples of different crystallinity is plotted as a function of temperature. One can identify a linear relationship between thickness and temperature from the graph in Figure 2.3.

Figure 2.3: Thermal expansion of PE as a function of temperature [27]
2.2. Complex Dielectric Permittivity

Electric permittivity is dependent on the polarizability of the material. The dielectric constant of LDPE is in the range of 2.25-2.35 and for HDPE it is in the range of 2.3-2.35 [22]. Complex dielectric permittivity consists of a real part $\varepsilon'$ and an imaginary part $\varepsilon''$, both of which are frequency dependent.

$$\varepsilon = \varepsilon' - i\varepsilon'' \quad 2.1$$

Also,

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad 2.2$$

tan$\delta$ is termed as the dissipation factor. It is the ratio of energy lost to the energy stored in an alternating field. Low values of tan$\delta$ is desirable for insulators as it indicates efficient insulation. It can also be expressed as,

$$\tan\delta = \frac{i_r}{i_c} \quad 2.3$$

Where,

$i_r$=Loss current (resistive)
$i_c$=Capacitive current or displacement current

For LDPE and HDPE the tan$\delta$ values are in the order of $5\times10^{-4}$ (1 MHz) [22]. The dissipation factor is also related to the morphology of the sample and it has been shown to decrease as a function of increasing crystallinity [28].

Dielectric spectroscopy measures the dielectric properties of a dielectric medium as a function of frequency [29]. It is calculated from the interaction of the material with external field. It characterizes the material properties by measuring the complex permittivity of the system over a range of frequencies. The energy storage and dissipation properties of the system are measured. In the case of an insulator like PE these properties are very crucial; thus one needs to understand their changes and the factors affecting them. There is different dielectric mechanisms studied to understand the way a medium reacts to the applied field. When an electric field is applied across a dielectric material the charges in the material are displaced from their equilibrium position; this process is called polarization.

Electric displacement in vacuum and applied electric field is related by the free space permittivity as,

$$D = \varepsilon_0 E \quad 2.4$$
The surface integral of displacement is the charge density. The rate change of charge density is the current in the circuit. Polarization in a material increases the displacement D by the total volume-density of dipole moments, \( P_t \), so that,

\[
D = \varepsilon E + P_t
\]

Thus, the total electric displacement can be expressed by the total of the contribution from free space and the polarization in the material. Polarization can be thought of as an increase in the permittivity, and the displacement can be expressed as the function of the effective permittivity \( \varepsilon \). But again if all the polarization is not instantaneous, then it cannot be included into a single effective permittivity. In that case the free-space permittivity together with the instantaneous polarization can be treated as a single value of permittivity \( \varepsilon_\infty \) and the slower remaining polarization \( P \) can be kept separate. Thus there are three ways to distribute the polarization to calculate the electrical displacement as [30],

\[
D = \varepsilon E
\]

\[
D = \varepsilon_\infty E + P
\]

The fastest mechanisms are the induced polarization due to the displacement of electrons and nuclei or displacements of ions in a lattice. The time for fast polarization is short corresponding to ultraviolet, visible or infra-red frequencies; fast polarization has little or no temperature dependency. Slower polarization mechanisms give rise to dynamic dielectric response at the frequencies met in electric circuits; slower polarizations are dipolar, carrier-dominated and interfacial polarizations [30].

The dynamic polarization mechanisms measured as dielectric response are described by the dielectric response function, \( f(t) \). This relates a dielectric’s polarization \( P \) at time \( t \) to the applied electric field \( E \) throughout history [30],

\[
P(t) = \varepsilon \int_0^\infty f(\tau)E(t-\tau)d\tau
\]

The Fourier transform \( \mathcal{F}\{\cdot\} \) of \( f(t) \) is a more convenient description [30],

\[
\chi(\omega) = \chi'(\omega) - i\chi''(\omega) = \mathcal{F}\{f(t)\}
\]

Where \( \chi(\omega) \) is known as the susceptibility, describing the relation of polarization to applied field as functions of frequency,

\[
P(\omega) = \varepsilon \chi(\omega)E(\omega)
\]
From which the total displacement due to this dynamic polarization and the prompt response is,

\[ D(\omega) = E(\omega)[\varepsilon + \varepsilon'\chi'(\omega) - i\varepsilon'\chi''(\omega)] \]  \hspace{1cm} (2.10)

The complex value of \( \varepsilon(\omega) \) can be split into real and imaginary parts as follows,

\[ \varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \]  \hspace{1cm} (2.11)

Where \( \varepsilon'(\omega) \) denotes the component of the real permittivity and \( \varepsilon(\omega) \) denotes the loss. The imaginary part of susceptibility makes it possible to describe a delayed response; the delayed response implies dissipation of energy, a dielectric loss due to polarization mechanisms takes a significant time on the scale of the frequency being studied [30]. In fact, a change of \( \chi'(\omega) \) with \( \omega \) (dispersion) is always accompanied by a nonzero value of \( \chi''(\omega) \), given a linear and causal dielectric response function [31]. This is due to the Kramers-Kronig relations between real and imaginary parts of Fourier transforms; these relations are used to calculate real part from the imaginary and vice versa of a response function. The real and imaginary parts of susceptibility \( \chi(\omega) \) describe respectively the peak stored energy in the material in a cycle and the mean energy dissipation per radian [32].

In real life application and testing of equipment and samples it is difficult to measure the field quantities directly. Instead a convenient concept is to measure the geometric capacitance \( C_0 \) also denoted as vacuum capacitance. This is the capacitance that a pair of electrodes would have in free space; if they are instead surrounded by homogeneous dielectric of permittivity \( \varepsilon(\omega) \), the complex capacitance \( C(\omega) \) is [30],

\[ C(\omega) = C'(\omega) - iC''(\omega) = C_0\varepsilon(\omega) \]  \hspace{1cm} (2.12)

In this thesis the real, component \( C'(\omega) \) is referred to as capacitance and the imaginary component \( C''(\omega) \) as loss. Hence the dissipation factor \( \tan\delta \) is calculated as,

\[ \tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{C''}{C'} \]  \hspace{1cm} (2.13)

Where \( \delta \) is the dielectric loss angle. In this work the real and imaginary values or capacitance will be measured to indicate the dielectric property of PE.
Chapter 3

3. Experimental Setup

In this section the set up used for different experiments will be introduced. There are mainly four steps of the whole experimental process. These are sample manufacturing, annealing, and testing the dielectric and morphological properties. They are carried out by the following instruments.

3.1. Dielectric Spectroscopy

Dielectric spectroscopy is carried out with the combination of a few instruments. The set up used for dielectric spectroscopy and their use are explained shortly below.

3.1.1. IDAX 300

Dielectric spectroscopy is used as the measure of complex permittivity of the polyethylene samples in this thesis. A Megger IDAX 300 was used for measuring the dielectric response of the samples. The IDAX 300 contains all components to supply sinusoidal voltages at amplitude up to 200 V and all frequencies from 100 µHz to 10 kHz, and to measure this voltage and current through the test object, performing Discrete Fourier Transform (DFT) to present the results in the frequency domain [33]. An external amplifier can be used with the equipment if higher voltage is required for the testing. The interface software version 4.0.1 and a control program [34] were used to take all measurements with this equipment.

![IDAX 300 front panel](image)

Figure 3.1: IDAX 300 front panel

Some additional information about calibrating the IDAX 300 has been included in the IDAX Calibration of Appendix A of the report.
3.1.2. High Voltage Unit (HVU)

IDAX 300 is compatible with a Trek ± 30 kV amplifier unit. When higher voltage than 200 V is required it can be used as an external source to feed the voltage. As initially it was assumed that the measurement could have strong voltage dependency it was planned to use the Trek HVU for all measurements. It takes a ±10 V input signal and gives regulated output voltage with a gain of 3000. The highest current is 40 mA for the HVU [33]. This unit can generate high voltage or high frequency; when used with IDAX the highest frequency it can generate is 100 Hz. It is connected to the IDAX through a communication cable and can supply the voltage to the test object by a high voltage cable.

![Figure 3.2: TREK high voltage amplifier and voltage divider](image)

3.1.3. Electrode

Low loss measurements of materials such as PE require a large surface area or thin samples in order to produce a sufficiently high capacitance. The bigger surface area solved the problem with very small geometric capacitance measurements. After manufacturing the electrode it was casted in epoxy. Initially the top high voltage electrode was cast with hard epoxy and the gap between guard and measure was filled with softer silicon rubber like epoxy, the reason was that the soft rubber would compress under the pressure of the high voltage electrode and provide a good contact surface with the sample. But the soft epoxy surface couldn’t be ground to get a very smooth surface so later it was replaced by hard epoxy and the electrode was ground to get a plane surface. To get correct measurements it is of utmost important to get a plane surface (not to confuse between shiny and plane), otherwise one could get unrealistic measurement values. Even a gap that is not visible with eye can cause significant error in measurements, so it is necessary to calculate relative permittivity from the geometric
capacitance after measurements and make sure there is no significant air gap between the electrodes and test object.

Figure 3.3: Electrode design [35]

Figure 3.4: Guarded low voltage electrode (left) and high voltage electrode (right)

The test object is kept between the two electrodes. The relative permittivity was found to be in the range on 2.22-2.29 for PE samples which is realistic value for LDPE and confirms a good contact surface and minimum air gap between electrode surface and the sample.
After casting the electrode with epoxy the next step was to test the highest voltage the system can reach without any partial discharge occurring. It was intended to go to as high voltage possible because that would allow observing any voltage dependency of the material property.

The electrode setup was then tested in different conditions to reach high voltage; the details of those experiments are included in Electrode Setup of Appendix A of the report.

3.2. Differential Scanning Calorimetry (DSC)

The goal of Calorimetry is to measure heat exchange. Heat exchange in a material is related to the temperature change and thus temperature can be used as a measure of the amount of exchanged heat. Chemical and physical transitions are generally coupled with heat consumption or production, thus Calorimetry can be used to study such processes. DSC is a more precise and modern version of the classic Calorimetry. It can be defined as,

‘Differential Scanning Calorimetry (DSC) means the measurement of the change of the difference in the heat flow rate to the sample and to a reference sample while they are subjected to a controlled temperature program.’ [36]

Differential scanning Calorimetry is a well-established method used in different fields of science and technology to study the properties of materials. Measurement values obtained by DSC allow heat capacity, heat of transition, kinetic data, purity and glass transition to be determined. DSC curves serve to identify substances, to set up phase diagrams and to determine degrees of crystallinity [36]. In this work DSC will be used to measure the crystallinity of the PE samples as an indicator for the morphological changes. DSC measures the change in property of the sample namely the heat flow rate change by the alteration of sample temperature. Temperature difference is imposed on the sample by external means, so in all DSC measurement there must also be a temperature profile. There are two types of DSC namely,

- Heat flow DSC
- Power compensation DSC

The common for all DSC methods is that it compares the heat flow of two slightly different samples. A common DSC setup is shown Figure 3.5,
Figure 3.5: Common DSC setup [36]

1-Disk
2- Furnace
3- Lid
4- Differential thermocouple(s)
5- Programmer and controller
S- Crucible with sample substance
R- Crucible with reference sample substance
Φ FS- Heat flow rate from furnace to sample crucible
Φ FR- Heat flow rate from furnace to reference sample crucible
K- Calibration factor.

From DSC measurement a curve of the heat flow vs time or temperature is obtained. Physical properties can be calculated by interpreting this curve in Figure 3.6.

Figure 3.6: DSC output curve [36]
DSC measurements are operated by a control program for changing the temperature with time to get the varied heat flow and physical change of the sample. Prior to the experiment a control method should be designed. There are two types of mode of operation [36],

- Constant heating rate
  - Isothermal
  - Scanning mode
  - High speed scanning
- Variable heating rate

In this thesis a control cycle with constant heating rate was used with combination of isothermal and scanning mode. The details of the method will be discussed in the later chapters.

### 3.2.1. DSC Equipment

A Mettler Toledo DSC 1 thermal analysis equipment was used in this work to get the DSC related measurements at KTH Polymer and Fiber Technology department. This is standard equipment used for thermal analysis of polymers. The interface and operation was fairly easy and user friendly. The temperature range is -150 °C - 700 °C for this instrument and it has a heating rate range from 0.02 to 300 K/min [37]. 34 samples can be put in for analysis in the equipment at the same time. Thermal analysis software is included with the system to analyze the results, it was used to analyze and calculate the crystallinity from the samples.

![DSC equipment](image37.jpg)

Figure 3.7: DSC equipment [37]
3.2.2. DSC Testing Method

As mentioned earlier in order to find crystallinity from DSC experiments a certain heating profile needs to be used. A series of experiments and meetings were conducted to find a suitable method for the DSC tests. Finally a control cycle with constant heating rate was used in combination of isothermal heating of the sample.

![DSC method, temperature profile](image)

Figure 3.8: DSC method, temperature profile

The method consists of five segments, two isothermal and three constant heating segments. First the samples are cooled quickly from room temperature to -70 °C and that temperature is maintained for a few minutes and then the heating is started from -70 °C to 180 °C. The sample is well melted at around 110 °C. The higher temperature is reached to get a steady baseline. 180 °C is maintained for a few minutes and then the sample is cooled down to room temperature again. Samples of 2-3 mg were used in 40µl cups by piercing a hole on the cup lead. A nitrogen environment was used in the whole measurement process.

With this cycle, curves like the Figure 3.9 are obtained and are used to find the crystallinity. The focus of interest is around the melting peak of the curve; at the melting point all the crystals are turned into an amorphous PE melt. Now if all the heat required to convert all the crystals of the sample into amorphous state can be calculated and divided by the heat of fusion of 100 % crystalline PE, the percentage of crystalline part of the samples can be found. This kind of curve relating the heat flow and temperature can be used to calculate the total heat required to melt all the crystals of a particular sample.
3.2.3. Determining the degree of crystallinity

DSC is widely used to determine the crystallinity level of semi crystalline polymer materials. The simplest way is to relate the heat of fusion of the sample to the heat of fusion of the same material with known crystallinity. The main challenge in this process is to fix the lower and upper integration limit to find the total heat required to melt all the crystals of sample under consideration. The upper limit can be taken after the melting point is reached. But deciding upon a lower limit is tricky, as often the polymer starts melting much before the actual melting temperature is reached. And with samples of different crystallinity this lower limit is changed. And again the crystallinity and heat of fusion are dependent on temperature. A simple way to solve this for the same kind of sample is to use a fixed integration limit for all samples and a fixed reference value of heat of fusion of fully crystallized sample of the same material [36]. In this thesis a lower limit for integration has been considered as -30 °C (243K) [38].

There are also different methods of calculating the crystallinity from the DSC curve. In this work the total enthalpy method has been used [39] [40] [41] [42]. In this method the crystallinity is calculated by the following simple formula,

\[
W_c = \frac{\Delta h_{\text{exp}}}{\Delta h_f(T) - \int_{T_1}^{T_m} (C_{pa}(T) - C_{pc}(T))dT} \times 100
\]

Where,

\( W_c \) = Crystallinity
\( \Delta h_{\text{exp}} \) = Enthalpy of the test sample, area under the heat flow curve
\( T_m \) = Desired temperature to find the crystallinity, 290 K
\( T_1 \) = Lower limit of integration, 243 K
\( \Delta h_f(T) \) = Heat of fusion of 100% crystallized PE, 290 J/g [43] used in this thesis
\[ C_{pa}(T) = \text{Heat capacity of amorphous PE, temperature dependent} \]
\[ C_{pc}(T) = \text{Heat capacity of crystalline PE, temperature dependent} \]

\( C_{pa} \) and \( C_{pc} \) values are integrated from the lower temperature limit \( T_1 \) to the temperature intended to calculate the crystallinity \( T_m \) to find the correction factor in the formula. All crystallinity values are calculated at 290 K. \( C_{pa} \) and \( C_{pc} \) values are taken from Table 4 of reference [44], and the value of the integration is calculated as 28.65 J/g. If a certain sample has \( \Delta h_{\text{exp}} = 124.745 \text{ J/g} \), the crystallinity would be,

\[
W_c = \frac{124.7445}{293 - 28.65} \times 100 = 47.37\%
\]

3.3. Polymer Press

Samples were prepared using a Fontijne Grotnes TP 400 hydraulic press at KTH Polymer and Fiber Technology department. This press is specialized for making polymer samples with precise control techniques. The maximum temperature that could be reached in this press is 400 °C and the maximum press force is 400 kN. The press has in-built water cooling and air cooling systems for cooling down samples after pressing. The details of sample preparation and press are described in the next sections.

Figure 3.10: Polymer press and front panel
3.3.1. Sample Preparation

Samples for the tests were prepared by pressing round plate samples from PE granulates received from ABB HVC. The pressing processes were conducted with the polymer press at KTH polymer and fiber technology department. The procedure of making samples from granulates is as Figure 3.11,

![Figure 3.11: Procedure for making PE samples from granulates](image)

The tricky part of this process is pressing the sample in the hot press. Granulates are put between two metal plates and two sheets of polyethylene terephthalate (PET, Mylar) or Polytetrafluoroethylene (PTFE, Teflon) and inside a metal ring. The setup can be understood from the pictures below in Figure 3.12. A PET sheet is put above a metal plate and ring is put on the top of the PET, and the PE granulates are put inside the ring, and another piece of PET is then put above the PE granulates and the other metal plate is put on the PET sheet. The whole setup is then put inside the press to make samples.

![Figure 3.12: Using press plates, ring and PET sheets for press](image)

The metal plates and rings were manufactured for this project, due to the fact that very smooth plate was required to get good working samples, because samples having even small cavities on the surface could possibly give difference in measurements and it would be difficult to
compare results. The samples were made a little bigger (14 cm diameter) than the electrodes to make sure that it covers the electrode surface properly. The pressed samples look like Figure 3.13.

![Pressed PE sample](image)

Figure 3.13: Pressed PE sample

After pressing the samples are wrapped in aluminium foil and preserved in freezer at 0 °C to make sure that the morphology of the sample is not changing. A precise press schedule for the polymer press was followed throughout the thesis to make samples; the steps in the test schedule are mainly consisting of the pressure and temperature profiles.

**Temperature profile:**

- Linear heating from 25 °C to 130 °C in 12 minutes
- Keep at constant temperature 130 °C from 18 minutes
- Linear cooling from 130 °C to 25 °C in 9 minutes, or quenching when the samples reaches at 90 °C
Figure 3.14: Temperature profile

**Pressure profile:**

- Constant pressure of 20 bar for 12 minutes
- Constant pressure of 200 bar for 18 minutes
- Constant pressure of 200 bar for 9 minutes

It is important to maintain pressure during the cooling of the sample.

Figure 3.15: Pressure profile

It is recommended to use PET sheets instead of Teflon to cover the stainless steel press plates for this test schedule and PE granulates, because when granulates are at solid at room temperature, 20 bar pressure is enough to make spots on the relatively soft Teflon sheet which will eventually make defective surface of the final sample. In case of PET no such phenomenon is observed.
3.4. Oven

A heraeus vacuum oven was used to perform all the annealing. The oven was connected with a Eurotherm 3501 temperature controller to measure and control the temperature.

![Vacuum oven](image)

**Figure 3.16: Vacuum oven**

An important issue that was needed to be taken into account when looking for very precise annealing temperature is the temperature overshoot of the oven. While trying to attain a higher temperature with the oven, it initially goes to a higher temperature and then takes time to settle down to the desired temperature. Any kind of annealing should be done after the temperature is settled to the desired value. Otherwise the sample will be annealed initially at a higher temperature and that would affect the overall crystallinity.

![Annealing temperature profile](image)

**Figure 3.17: Annealing temperature profile**
In the Figure 3.17 an example of such phenomenon is given, when trying to reach 75 °C from 65 °C the oven temperature first reaches up to 85 °C and then settles to 75 °C after around 40 minutes. Thus any annealing intended should be performed after 40 minutes of increasing the temperature value in the oven controller. In this thesis the oven was pre heated and a waiting time of 60 minutes was used before any sample was put in the oven for annealing to make sure that the required temperature is achieved.

3.5. Micrometer

A Mitutoyo Absolute digital micrometer was used to measure the thickness of the samples prepared, as the geometric capacitance is related to the thickness of the samples. It was important to make corrections for sample thickness in the dielectric measurements.

![Digital micrometer](image)

Figure 3.18: Digital micrometre
Chapter 4

4. Design of Experiments and Results

The problem statement consists of three factors, namely the heat treatment, morphological changes and the dielectric properties. To influence or measure these three properties three equipment or tools were used: to introduce the heat treatments an electric oven, to see the change in morphology due to heat treatment DSC; and finally to see the change in electrical property dielectric spectroscopy the IDAX system. Also the thickness changes due to the heat treatment were also measured with a digital screw micrometer. The test procedure can be expressed by the following chart in Figure 4.1.

![Chart showing the experiment design process](image)

Figure 4.1: Basic work process of sample testing

Now there are also other variables that come within these main three variables. For example, the sample manufacturing process also could be different and add another variable to the experiment.

<table>
<thead>
<tr>
<th>Sample preparation</th>
<th>Heat Treatment</th>
<th>Sample thickness</th>
<th>Dielectric measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slowly Cooled</td>
<td>Annealing temperature</td>
<td>Due to production procedure</td>
<td>Voltage</td>
</tr>
<tr>
<td>Quenched</td>
<td>Annealing time</td>
<td>Due to annealing</td>
<td>Frequency</td>
</tr>
<tr>
<td>Thickness</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.2: Factors for experiment design
Some additional factors that were considered when preparing the test matrix are listed in Figure 4.2.

4.1. Sample preparation

The initial plan for sample preparation was to cool the sample by the built in water cooling system of the polymer press. This cooling process takes around 9 minutes, which means a certain level of crystallinity can be achieved by this method. The main test of this work has been conducted on samples that were cooled inside the press under pressure; supposedly this would allow making samples having similar properties. Another option to get to an even lower level of crystallinity was to quench the sample in water at room temperature and cool the sample very quickly. The samples were taken out of the oven at 90 °C so they already have had a fairly solid formation and then they were quenched. This idea had some flaws, so it was doubted that every time exactly similar samples could not possibly be prepared by this method for the following reasons,

- Not cooling samples under pressure
- The water temperature was not regulated
- Samples cannot be taken out of the oven at exactly 90 °C every time

This method of sample preparation was only used for a few samples and used as a supporting experiment together with the main tests. But this would surely provide insight and confidence in the finals results as for this type of sample preparation a different level of crystallinity was achieved.

The goal of the thesis was to work on relatively thicker samples. Initially 0.5 mm and 1 mm thick samples were considered. For the thinner 0.5 mm sample the geometric capacitance would be higher and the C’ would be higher too, with 1 mm sample these values would be lower.
Figure 4.3: Comparison between C'' of 0.5 mm and 1mm samples

Figure 4.3 shows C'' measurements for 0.5 mm and 1 mm samples at 500 V, both samples were not annealed and the same pattern is noticed, but the thinner sample has twice as high magnitude of loss as expected.

If thicker samples (2 mm and 3 mm) were used the C'' measurements would be very small and the IDAX system would have difficulties in measuring the values. Keeping in mind the goal of the thesis to measure on relatively thick samples, and the measurement limit of IDAX 300, the thickness of 1 mm was selected to conduct the final tests.

4.2. Thickness change of the samples

The values and differences that were targeted to be observed in this thesis work were very small in magnitude, thus minute details had to be paid in all measurement parameters. It was observed that the thickness of the samples produced was not exactly the same, which might result in misinterpretation of test results if not measured and corrected. The geometric capacitance and relative permittivity is related to the thickness of the test object. Even though the same press schedule was followed for different samples the samples come with different thickness with a standard deviation of around 0.3%. To compare the results of dielectric spectroscopy from different samples the results should be corrected for the thickness difference. The thickness of different samples for a particular test is shown in Figure 4.4,
The thickness measurement of the samples can be a little tricky, because the samples are not uniformly thick in all areas. The reason is that the press is not absolutely leveled to the ground, resulting in that one side of the sample will become a bit thicker than the other side. This has been demonstrated by measuring thickness around different points of the sample, and by cutting few samples through the middle and measuring the thickness through the center of the sample.

Figure 4.4: Average thickness of different samples in a test

Figure 4.5: Thickness through the axis of the sample for two samples
For example the thickness data in Figure 4.5 was obtained by cutting two samples and measuring their thickness through the center of the sample. As mentioned earlier the samples were 14 cm in diameter, and measurements were taken from the centre in 2 cm intervals along both sides. Now it is noticeable that the samples are actually thicker in one side, while trying to measure the thickness of the sample one needs to take few measurements across the whole sample and take the average. In this thesis six measurement points were taken in each sample and the thickness is calculated by their average.

The thickness variation of the samples from the press is random and there was no particular pattern. But it was also observed that the samples changed their thickness during the annealing process. PE is expected to get relaxed and thicker with heat treatment [45] but to observe this phenomenon in such a sample was interesting.

After observing the issue of the thickening of the PE samples with annealing time and temperature, this effect was measured extensively. The thickness change with annealing time and temperature was studied on small circular samples of 1mm thickness and 3.4cm diameter. Five samples were put in the vacuum oven for each temperature 22 °C, 35 °C, 50 °C, 65 °C, 70 °C and 90 °C for annealing and the thickness change was studied. The benefits of using small sample are that they can be measured precisely in the same spots and it would be easier to observe the changes. The fact that the sample swells with annealing is also visible in the above Figure 4.5, it is noticeable that the 72 h annealed sample has higher thickness in all points. The spectroscopy results had to be corrected for this change in thickness, and the sample thickness had to be measured immediately before conducting the spectroscopy to get the values. Subsequently the diameters of sample were also measured as one expects a decrease in diameter with increasing thickness.

In Table 4-1 the change in thickness is given with different temperature and time,

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time (h)</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>24</th>
<th>48</th>
</tr>
</thead>
<tbody>
<tr>
<td>22 °C</td>
<td>1</td>
<td>1.000157</td>
<td>0.99985</td>
<td>1.000158</td>
<td>1.00027</td>
<td>1.002809</td>
<td>.999</td>
<td></td>
</tr>
<tr>
<td>35 °C</td>
<td>1</td>
<td>1.000618</td>
<td>0.999814</td>
<td>1.00025</td>
<td>1.001359</td>
<td>1.006849</td>
<td>1.00814</td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>1</td>
<td>1.003279</td>
<td>1.005064</td>
<td>1.005137</td>
<td>1.006647</td>
<td>1.009641</td>
<td>1.012027</td>
<td></td>
</tr>
<tr>
<td>65 °C</td>
<td>1</td>
<td>1.00818</td>
<td>1.008518</td>
<td>1.009392</td>
<td>1.010789</td>
<td>1.012184</td>
<td>1.013136</td>
<td></td>
</tr>
<tr>
<td>70 °C</td>
<td>1</td>
<td>1.008224</td>
<td>1.0109</td>
<td>1.011977</td>
<td>1.013657</td>
<td>1.01473</td>
<td>1.015082</td>
<td></td>
</tr>
<tr>
<td>90 °C</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.01608</td>
<td></td>
</tr>
</tbody>
</table>

The change of thickness with temperature was measured in different temperature and time. The measurement at 90 °C was taken as an extreme case and maximum change was expected from this measurement. If the data set is observed one can notice an exponential characteristic. In fact these data can be modelled in a general form as,
\[ f(t) = a - (a - 1) \times e^{-b \cdot t} \]

4.1

Where, \( a \) and \( b \) are constants, and \( t \) is temperature. Figure 4.6 shows the model together with measurement data.

Figure 4.6: Modelling of the thickness change relative to initial thickness

The constants \( a \) and \( b \) are obtained for the model are shown in Table 4-2,

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( a )</th>
<th>( b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>22 °C</td>
<td>1.0001</td>
<td>0.01016</td>
</tr>
<tr>
<td>35 °C</td>
<td>1.011</td>
<td>0.03066</td>
</tr>
<tr>
<td>50 °C</td>
<td>1.012</td>
<td>0.1368</td>
</tr>
<tr>
<td>65 °C</td>
<td>1.013</td>
<td>0.46</td>
</tr>
<tr>
<td>70 °C</td>
<td>1.0148</td>
<td>0.46</td>
</tr>
<tr>
<td>90 °C</td>
<td>1.016</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Now if constants \( a \) is plotted with temperature the following Figure 4.7 is obtained,
Figure 4.7: Values of constant $a$ with temperature and curve fit

It is observed from Figure 4.7 above that $a$ have a temperature dependency, which can be fit very well with an exponential function. Again if $b$ is plotted against time the following Figure 4.8 is found,

Figure 4.8: Values of constant $b$ with temperature and curve fit
It is observed from Figure 4.8 above that $b$ also have a temperature dependency, which can be fit very well with an exponential function up to 65 °C and a constant value after that. The idea of modeling the constants $a$ and $b$ is that, it would be possible now to predict the magnitude of sample thickening for different annealing temperature and time.

Now if the thickness change is plotted with temperature for different annealing time the following Figure 4.9 is obtained,

![Graph showing thickness change with temperature and time](image)

Figure 4.9: Thickness (Normalized) with annealing temperature

It is observed from Figure 4.9 that with higher annealing temperature the thickness increases according to the theory explained in 2.1.3 and Figure 2.3. With longer annealing time the graphs shift upwards which is also expected.

It is also expected to get a decreased diameter with increasing thickness of a sample, as the volume would remain fairly constant, and therefore the diameters were also measured. As shown in Table 4-3 the diameter data shows decrease and a trend can be recognized with higher temperature.

### Table 4-3: Sample diameter change relative to initial thickness

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>24</th>
<th>48</th>
</tr>
</thead>
<tbody>
<tr>
<td>22 °C</td>
<td>1.000</td>
<td>0.999</td>
<td>1.000</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
</tr>
<tr>
<td>35 °C</td>
<td>1.000</td>
<td>0.999</td>
<td>1.000</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
</tr>
<tr>
<td>50 °C</td>
<td>1.000</td>
<td>0.999</td>
<td>1.000</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
</tr>
</tbody>
</table>

53
The data from Table 4-3 is shown in Figure 4.10 below,

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Diameter change</th>
<th>Diameter change</th>
<th>Diameter change</th>
<th>Diameter change</th>
<th>Diameter change</th>
<th>Diameter change</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 °C</td>
<td>0.998262</td>
<td>0.997683</td>
<td>0.997539</td>
<td>0.997828</td>
<td>0.998263</td>
<td>0.998697</td>
</tr>
<tr>
<td>65 °C</td>
<td>0.997686</td>
<td>0.996819</td>
<td>0.995807</td>
<td>0.996095</td>
<td>0.996674</td>
<td>0.997542</td>
</tr>
<tr>
<td>70 °C</td>
<td>0.997394</td>
<td>0.996677</td>
<td>0.996235</td>
<td>0.996815</td>
<td>0.996091</td>
<td>0.996091</td>
</tr>
<tr>
<td>90 °C</td>
<td>1.000000</td>
<td>0.999674</td>
<td>0.999999</td>
<td>0.999999</td>
<td>0.999999</td>
<td>0.999999</td>
</tr>
</tbody>
</table>

Figure 4.10: Diameter change of samples relative to initial thickness

The thickness and diameter measurement graphs for individual samples at different temperature are included in the IDAX Calibration in the Appendix B of the report.

4.3. Morphological Effect of Heat Treatment

The heat treatment had two variables to decide on, firstly the temperature and secondly the time for annealing. Initially an annealing temperature of 80 °C has been agreed and few tests were conducted with annealing time of 0, 1, 2, 4, 8, 16, 32 and 72 h. But after the dielectric tests with these samples no clear trend was found. The idea was to try another annealing temperature because it could be that the annealing process saturated very quickly at 80 °C and the time interval for annealing was too small to see any clear trend. Thus an annealing temperature of 50 °C was used for the final tests. The goal was to see the effect of annealing in a slower time frame.
The effect of annealing can be seen in the DSC heat flow curve in Figure 4.11, the black curve in the figure is for a sample that was not annealed and the red curve is for an annealed sample. And the annealing was conducted at 80 °C in this case, thus in the red curve an additional peak is seen at 80 °C which indicates the growth of crystals at that temperature. In the black curve no such peak is visible because the sample was not annealed.

![DSC heat flow curve](image)

Figure 4.11: Effect of annealing on heat flow curve

A time interval of 0, 1, 2, 4, 8, 16 and 64 h was used in the main tests to observe the effect of different levels of annealing, and for the tests later the intervals were determined observing the results of previous sweeps. Samples were annealed at 50 °C for different time periods. Pieces of samples were cut for DSC test right after they were manufactured and after they were annealed. There were six levels of annealing and thus there are six 6 levels of crystallinity. For each level of crystallinity there were two different samples for two voltages, and two pieces were cut from each sample and preserved for DSC. To get a good reliable data for each level of crystallinity four tests were finally conducted for each level and the average was taken. The crystallinity test results are given in Table 4-4,

<table>
<thead>
<tr>
<th>Annealing Time (h)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>44.81</td>
</tr>
<tr>
<td>1</td>
<td>45.01</td>
</tr>
<tr>
<td>2</td>
<td>46.99</td>
</tr>
<tr>
<td>4</td>
<td>51.29</td>
</tr>
<tr>
<td>16</td>
<td>53.29</td>
</tr>
<tr>
<td>64</td>
<td>56.80</td>
</tr>
</tbody>
</table>
The results from DSC tests can be appreciated if plotted in a graph with annealing time and with an exponential function in the form of

\[ f(t) = p e^{qt} + r e^{st} \]  \hspace{1cm} (4.2)

Where, \( p, q, r, s \) are constant and \( t \) is temperature. Curve fit and the measurement data is shown in Figure 4.12,

![Graph showing crystallinity with different annealing time data and exponential curve fit](image)

Figure 4.12: Crystallinity with different annealing time data and exponential curve fit

Crystallinity at 0 h annealing time is the crystallinity of the samples that are not annealed at all. With annealing time the crystallinity increases, as expected from the theoretical explanations, the crystallinity values from 4, 16 and 64 h annealing are in a similar range. This exponential behaviour is also expected as the crystallization process slows down with time [8] and a particular material can only reach certain crystallinity even if annealed for an infinite amount of time.

Another phenomenon that could be observed from the DSC test data is the change in melting peak of the samples with different annealing time. The average peak temperature values for different levels of annealing were also taken similarly to that of crystallinity stated above, the following

Table 4-5 shows the average Peak melting temperature of samples with annealing time,
Table 4-5: Peak melting temperature with different annealing time

<table>
<thead>
<tr>
<th>Annealing Time (h)</th>
<th>Peak Melting Temperature $T_{\text{melt}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>385.222</td>
</tr>
<tr>
<td>1</td>
<td>385.285</td>
</tr>
<tr>
<td>2</td>
<td>385.403</td>
</tr>
<tr>
<td>4</td>
<td>385.498</td>
</tr>
<tr>
<td>16</td>
<td>385.538</td>
</tr>
<tr>
<td>64</td>
<td>385.543</td>
</tr>
</tbody>
</table>

The lamella thickness can be predicted based on the melting temperature received from DSC measurements by using the Thomson-Gibbs equation [46].

$$T_{\text{melt}} = T_m^\circ \left(1 - \frac{2\sigma_f}{\Delta h_f L}\right)$$  \hspace{1cm} (4.3)

Where,

- $T_{\text{melt}}$= Melting temperature
- $T_m^\circ$ = Equilibrium melting temperature, 145.8 °C for PE [46]
- $\sigma_f$ = Surface free energy, 90 mJ/m$^2$ for PE [47]
- $\Delta h_f$= Heat of fusion of 100% crystallized PE, 290 J/g [43]
- $L$=Lamellar thickness

The temperature values should be used in Kelvin, and the Heat of fusion values should be used for per unit volume for finding $L$ from Equation 4.3. Using values of $\sigma_f$, $\Delta h_f$ and expressing $L$ in nm in Equation 4.3 the following is obtained,

$$T_{\text{melt}} = T_m^\circ \left(1 - \frac{0.6207}{L}\right)$$  \hspace{1cm} (4.4)

Values of lamellar thickness calculated from Equation 4.4 and Table 4-5 is given in the following
Table 4-6: Lamellar thickness with different annealing time

<table>
<thead>
<tr>
<th>Annealing Time (h)</th>
<th>Lamellar Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>77.42</td>
</tr>
<tr>
<td>1</td>
<td>77.56</td>
</tr>
<tr>
<td>2</td>
<td>77.84</td>
</tr>
<tr>
<td>4</td>
<td>78.06</td>
</tr>
<tr>
<td>16</td>
<td>78.15</td>
</tr>
<tr>
<td>64</td>
<td>78.16</td>
</tr>
</tbody>
</table>

The calculated thickness values agree with values found in literature [48] for similar melting temperature. These data can be plotted to get Figure 4.13, which shows similar exponential characteristic as Figure 4.12.

Figure 4.13: Lamella thickening with annealing time

The results from the DSC tests confirms that the annealing process has had an effect on the crystallinity by three means, firstly the results shows increase in crystallinity in Table 4-4 and secondly the DSC heat flow curves as in Figure 4.11 show a peak and finally, as mentioned before at the temperature at which it was annealed. Finally from Table 4-6 it is observed that the lamellae get thicker with annealing time.
4.4. Dielectric measurements

This was the most important measurements of the work; the samples had to be tested with the IDAX 300 to see how the morphological and heat treatment changes the dielectric measurements. The detailed set up and the results for dielectric spectroscopy are included in this section.

4.4.1. Measurement Parameter Selection

There were two factors in deciding the dielectric measurements, the frequency range of the sweep and the voltage levels. The frequency range is in the higher side is constrained by the high voltage unit used with the IDAX, as the HVU could supply maximum 100 Hz at higher voltages in this particular test set up. The IDAX internal source can go to up to 10 kHz at 200 V, which was an option if very high frequency is required. The low frequency measurements are constrained mainly by time. Very low frequency points take a long time to measure and it would be suspected that if the samples were kept in room temperature for that long the morphology would change a lot by the time the frequency sweep is finished. The frequency range that was decided was \(10^3\) - \(10^2\) Hz when measuring with the HVU; for particular samples the low frequency range down to \(10^4\) Hz were reached with the HVU, and high frequency up to \(10^4\) Hz with the IDAX internal source.

The voltage level where the sweeps should be run was very important to determine. First one needs to investigate if there is actually any strong voltage dependency of the measurements. To study this, a few samples with different annealing times were tested at different voltage levels; first a sweep was run with a sample that was not annealed and another sweep with a sample that was annealed for 8 h with voltages 200 V, 500 V, 1000 V, 2000 V, 4000 V and 6000 V. The relative permittivity calculated from geometric capacitance, also C” from these two sweeps are given below in Figure 4.14,
As seen from the Figure 4.14 the relative permittivity calculated from the capacitance is fairly the same for all the voltage levels for this sample. The 200 V line is slightly lower than the others at higher frequency but settles to the similar values of the other voltage levels at lower frequencies.
In Figure 4.15 of C” the similar phenomenon is observed, the graphs are all at the same level, and they overlap each other except for very low frequency. This indicates that the conductivity at low frequency is voltage dependent.

Figure 4.16: Relative permittivity for different voltage levels (8 h annealing)

Figure 4.17: C” for different voltage levels (8 h annealing)
Almost exactly the same phenomenon is observed in the Figure 4.16, the graph of relative permittivity of the sample annealed for 8 h, there are no such big changes in permittivity, and one can identify a trend of higher permittivity with high voltage. But if now the next Figure 4.17, C” for 8 h of annealing is seen again no clear trend or voltage dependency can be observed. After these experiments it was concluded that the measurements do not have a strong voltage dependency and even if there is any that is not observable in this set up. For this reason the final measurements were taken at only two voltage levels as of 500 V and 2000 V, and that was also done to have repeatability of experiments rather than finding out effect of voltage on the dielectric measurements. In a few cases when it was intended to go to very high frequency, the internal source of IDAX was used with 200 V.

The temperature in the high voltage lab was logged and it was found to be fairly constant at 22.4 °C with variation of ±0.2 °C. A temperature log graph is included in Temperature log of HV laboratory in Appendix C of the report. The electrical tests were run at two voltage levels as mentioned before; additionally a few 200 V sweeps were performed. The relative permittivity was calculated for each sweep to make sure that the results are comparable. There are two series of tests conducted, the main test sequence with slowly cooled samples from the press and another variation with quenched samples.

4.4.2. Slowly Cooled Samples

These tests are the main results of the thesis. Results from this test is categorized as per different voltage levels and compared below.

200 V:
At 200 V it was possible to look into high and very low frequencies. In Figure 4.19 the 16 h annealed sample shows lower loss at lower frequency range. It is noticeable that the loss $C''$ appears to increase at high frequencies.

500 V:
Figure 4.20 and Figure 4.21 above shows the relative permittivity and $C''$ value for different samples annealed for different time periods. The relative permittivity increases with lower frequency which is expected, the loss reaches a maximum at $10^2$ Hz and decreases afterwards. But there is no clear trend recognizable of the $C''$ graphs with annealing time.

**2000 V:**

Figure 4.22: Relative permittivity at 2000 V
The behaviors of the graphs in Figure 4.22 and Figure 4.23 are almost similar to that of the previous figures. The 4 h annealed sample tend to be different and not following the general pattern of curves.

**Low frequency sweep in different voltage:**
In Figure 4.25 at very low frequencies higher values of $C''$ was measured, which could indicate initiation of conduction. The higher voltage curves starts having higher $C''$ at comparative higher frequencies. Again, there are not much distinguishable changes of $C''$ due to annealing.
4.4.3. Quenched Samples

In this series of tests quenched samples were used and annealing time periods of 0, 1, 2, 4 and 16 h were considered. All the samples were tested at 500 V and in addition two more samples of 0 h and 16 h annealing were tested at 200 V.

200 V:

![Figure 4.26: Relative permittivity at 200 V](image)

![Figure 4.27: C'' at 200 V](image)
The results are similar to the previous test. In the graphs of Figure 4.26 and Figure 4.27 above at 200 V and frequency range of $10^2$-$10^4$ Hz, difference in the annealing time do not show any change in the dielectric measurements.

500 V:

![Graph 4.28: Relative permittivity at 500 V](image)

![Graph 4.29: $C''$ at 500 V](image)
At 500 V again the similar pattern is observed. No clear trend for different annealing time can be observed from the measurements graphs of Figure 4.28 and Figure 4.29.

**Low frequency sweep at different voltages:**

![Graph showing relative permittivity and Capacitance](image)

**Figure 4.30: Relative permittivity down to $10^{-4}$ Hz**

**Figure 4.31: $C''$ at down to $10^{-4}$ Hz**

Again at very low frequencies the start of conduction can be observed from the Figure 4.31 measurements, this is also similar to what was observed in Figure 4.25.
4.4.4. Modelling of experimental data

The data found from the dielectric spectroscopy experiments was possible to model with Havriliak–Negami equation for dielectric relaxation

\[
\hat{\varepsilon}(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + (i \frac{\omega}{\omega_0})^\alpha} \beta + \frac{\sigma_{dc}}{i\omega \varepsilon_0}
\]  

4.5

Where,

\[\Delta \varepsilon = \varepsilon_s - \varepsilon_\infty,\]

\[\varepsilon_\infty = \text{High-frequency permittivity}\]

\[\varepsilon_s = \text{Low frequency static permittivity}\]

\[\sigma_{dc} = \text{Conductivity}\]

\[\alpha, \beta = \text{constants}\]

The values used for the modeling is as follows,

\[\varepsilon_\infty = 2.275\]

\[\Delta \varepsilon = 0.0252\]

\[\alpha = 0.5\]

\[\beta = 0.95\]

\[\sigma_{dc} = 2.4 \times 10^{-17} \text{ S/m}\]
This Figure 4.32 gives a comparison between the experimental results and modelling, it shows that the data obtained from the experiments are very close to the values obtained by modelling which confirms the fact that the data set from experiments are realistic and reliable.
Chapter 5

5. Conclusion

A few observations can be drawn from all the experiments conducted and the results presented in this report. The goals of this thesis can be restated again here as a reminder, the objective of this work was,

- To evaluate effect of morphological changes via thermal annealing on dielectric properties of polyethylene by experiments on plaque samples.
- To characterize and evaluate the effect of thermal annealing and other methods on the morphology of polyethylene.
- To study the correlation between morphology of polyethylene and its dielectric properties.

Samples of different thermal annealing were measured at different voltage levels, and from the figures in the Chapter 4 it can be concluded that the effect of annealing was not observable on the dielectric measurements in the frequency range $10^{-3}$-$10^{2}$ Hz. At lower frequencies down to $10^{-4}$ Hz some changes can be seen when the samples enter conduction region. But again the dielectric measurement method is not ideal for observing the changes in conductivity, so it can be concluded in the scope of this thesis that there is not a strong relation between thermal annealing and dielectric measurements.

The thermal annealing definitely have had affected the morphology of the PE samples, this is manifested by two observations. The change in crystallinity with annealing time and the appearance of small peak in the annealing temperature in the heat flow curve confirms that thermal annealing affected the morphology of the samples. Annealing also affected the thickness of the samples. The samples swell with higher annealing temperature and time. This was confirmed by the thickness experiment results.

The outcome of the thesis can be stated precisely with the following statements,

- Heat treatment significantly affects the morphology and the thickness of polyethylene samples
- Dielectric measurements of polyethylene after heat treatment (annealing) must be compensated for change in thickness
- Dielectric properties of polyethylene for the studied frequency range ($10^{-3}$-$10^{2}$ Hz) are not strongly affected by the morphological changes
Chapter 6

6. Future work

In this study only a few combinations and possibilities were implemented and tested. Quite a lot of research can be conducted in this field to understand the topic better.

In this thesis only sample of 1 mm thickness was studied in the final experiments. It would be interesting to see how these properties behave with even thicker samples. And annealing temperature of 50 °C was used for all experiments, if some other annealing temperature could be studied then it would be possible to draw a relationship between annealing temperature and crystallinity.

In this work only DSC was employed to study the change of morphology of samples, but increase in crystallinity percentage is not the only morphological change that is expected from heat treatment. The thickening of crystallites and their changes in orientation could have been studied if some other methods e.g. scanning electron microscope, x-ray scattering to observe morphological change could be employed.

And finally this test procedure could be employed to study some other insulating polymer.
7. Bibliography


[34] N. Taylor, Personal Correspondence.


Appendix A

In the appendix the experiments related to the setup of experiments and additional results are documented.

IDAX Calibration

When spectroscopy measurements were taken with the IDAX initially with an electrode of diameter 3.5 cm, it was observed that for PE sample the geometric capacitance and loss component were very small, so the complete control of the equipment behavior was needed to understand the output data and observe small changes. For that reason the control of the feedback components of the IDAX was changed, studied and different combinations were tried.

For measuring in small, very low loss materials where $C''$ is in the level of $10^{-14}$ F and the IDAX output curves for the $C''$ looked like a saw tooth (Figure A.2) and it was very difficult to see and identify the changes that were important for this project. Certainly the sudden changes in values of $C''$ in every decade of frequency was some sort of instrumentation error, and to get reliable data it had to be made sure that these instrumentation errors do not affect measurements. From the general trend of the measurements these so called ‘jump’ in the measurement in every decade of frequency was not acceptable. And the problem was severe when the values were in the range of $10^{-15}$ F.

To improve the situation it was decided to test with the reference capacitor in the lab, the capacitor is believed to have a very low loss which should remain similar for the range of frequency and hence the IDAX should measure the $C''$ for the capacitor as a straight line at around $10^{-15}$ F. The capacitor measurement also showed the saw tooth pattern and the IDAX feedback calibration was required to be adjusted to eliminate the saw tooth pattern.

The probable reason for this was the wrong calibration of the feedback capacitor. Previously few other combinations of different settings for the feedback were tried, for example trying to use only resistive feedback and only capacitive feedback, but it looked like the default (using mainly resistors) was the only option that was suitable for this purpose, but again it was not possible to get good measurements without any capacitor, thus it was decided to use the smallest capacitor ‘C6’ (100 pF) in the feedback and trying to change the calibration values of C6 in the IDAX calibration file to get desired output.

The control of feedback was set to manual to use the Capacitor C6 always and calibration editor was used to change the values. A capacitor model code [34] was use to understand the effect that the 4 parameters used in the model the capacitor and their effect on the measurement. Simulations were performed with the code to understand the parameter effects and subsequently measurements were performed to figure out the optimum calibration values and in the end it was decided that the best that was achievable was the following:
These constants are used in the calibration of the instrument, these values were changed in the IDAX calibration editor (more information look ref: [33]) and the results obtained with these parameters were evident in the C'' measurements of the reference capacitor, in the Figure A.1 the top red curve is the measurement with the original calibration and the lower blue curve is measurement after changing the values. Now in there is still a saw tooth pattern but at much lower values and thus less likely to distort measurements.

Figure A.1: Effect of calibration change on C'' values of reference capacitor

Later the measurement for the polyethylene sample was conducted to see the changes in the measurement due to the calibration. The Figure A.2 shows the difference, the curve shows that after the calibration it was possible to partially get rid of arbitrary jumps of data in every decade of frequency.
This calibration of the IDAX was not finally required when taking the measurement for the final experiments because the difficulty of measuring such small geometric capacitance and losses were tackled by constructing an electrode with a higher diameter, hence higher geometric capacitance of the test sample and higher loss. With the bigger electrode the losses measured were high enough so it was not important to worry about the errors in the range of $10^{-14}$ F and $10^{-15}$ F to be making serious effects on measurements. Nevertheless this section has been included in the report for anyone trying to measure very small losses ($10^{-15}$ F) with the IDAX in near future would face similar problems and this would guide to a way to solve problems related to low loss measurements.

**Electrode Setup**

**Effect of Increasing Pressure on the Electrode**

The easiest idea that could be implemented to increase the PD inception voltage of the electrodes was trying to increase the pressure on the electrodes to eliminate small air gaps between sample and electrodes. Two wooden plates and four screws were used to make a clamp around the electrodes and the goal was to increase the pressure on the electrode to remove any air pockets between the test object and the electrode surfaces, which presumably can limit maximum voltage attained by the electrode or can introduce errors in measurements. The dielectric response was measured at 40 Hz at different voltage levels. A partial discharge would increase the apparent values of $C''$ significantly and that was used as an indirect indicator of PD in the electrode. A 1 mm thick PE sample was used and the first test was run...
without the clamp. The voltage was increased from 3 kV up to 6 kV and both the geometric capacitance and $C''$ were recorded, the geometric capacitance was measured to make sure that the same test object is being used for the both tests. It can be observed from the Table A-1 that the $C''$ value changes significantly at 5 kV and thus indicating PD inception in the system. Now for the second test the electrodes were clamped between two wooden plates and the same test was conducted, but again it was observed that the PD inception voltage remained at 5 kV indicating that for this particular set up there was not effect of increasing pressure on the electrode and PD inception voltage.

Table A-1: Comparison of $C''$ values between unclamped and clamped electrodes

<table>
<thead>
<tr>
<th>Voltage (kV/mm)</th>
<th>3</th>
<th>3.5</th>
<th>4</th>
<th>4.5</th>
<th>5</th>
<th>5.5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unclamped</td>
<td>4.8688$\times 10^{-15}$</td>
<td>4.6212$\times 10^{-15}$</td>
<td>4.7633$\times 10^{-15}$</td>
<td>4.6141$\times 10^{-15}$</td>
<td>7.738$\times 10^{-14}$</td>
<td>3.311$\times 10^{-13}$</td>
<td>3.7952$\times 10^{-13}$</td>
</tr>
<tr>
<td>Clamped</td>
<td>5.2701$\times 10^{-15}$</td>
<td>5.3815$\times 10^{-15}$</td>
<td>5.9739$\times 10^{-15}$</td>
<td>6.2113$\times 10^{-15}$</td>
<td>7.0149$\times 10^{-14}$</td>
<td>4.8634$\times 10^{-13}$</td>
<td>4.2057$\times 10^{-13}$</td>
</tr>
</tbody>
</table>

**Oil Experiment**

The next experiment to increase the PD inception voltage was carried out by putting the whole experimental set up in transformer oil. The oil was degassed in vacuum to make sure that there were minimum air bubbles and humidity inside the oil. There were three objectives of this experiment,

- If the PD inception voltage increases in oil.
- If the sample changes if it is kept in oil for a long time, and
- If similar $C''$ measurements from the sample can be obtained if it is submerged in oil.

Three frequency sweeps in different voltage levels have been conducted to see the effect of using oil in the set up.

- Frequency sweep under normal condition.
- Frequency sweep submerging the setup in oil.
- Keeping the setup in oil for 20 h and observe if the $C''$ value changes.

The results from the experiments are shown in the following Figure A.3. Please note that the sample used was 0.5 mm in thickness.
From the Figure A.3 it is observed that the $C''$ values when the electrodes are submerged in oil changes drastically. Another issue with this setup is noticed if looked into the curves after keeping the setup in oil for 20 h, it seems that oil changes the property of PE sample and the $C''$ curves change with time too. Using oil in the experimental setup to get to higher voltages was not pursued after this experiment, even though higher voltages could be achieved by the setup before PD inception.

**Vacuum Experiment**

The next experiment carried out to increase the voltage limit of the electrodes was about trying to create a low pressure environment around the electrode. The idea can be easily explained by the well-known paschen curve for partial discharges.
It was assumed that there are small gaps between the test sample and electrode which make small air paths which make the partial discharge in the setup. Under normal air pressure the setup is on the right hand side of the minimum breakdown voltage of the Paschen curve. The X axis of the curve is pressure multiplied by distance, so if low enough pressure can be reached it could be possible to get to the left side of the Paschen minimum and on the left side very high voltage could be reached without any partial discharges. The electrodes were placed in a metal chamber with high voltage and measurement lids and a vacuum pump was used to create low pressure. The dielectric response was measured at 10 Hz at different voltage levels. A partial discharge would increase the measure C'' significantly, and that was used as an indirect indicator of PD in the electrode. A pressure gauge was connected to the chamber to get the values of pressure in the chamber and same tests were conducted in normal pressure, 220 mbar and 1.8 mbar. The test object was kept untouched to make sure the same capacitance was measured in all the tests. The results from three tests run in three different pressure levels are given in Table A-2 below,

<table>
<thead>
<tr>
<th>C'' (F)</th>
<th>Voltage (kV/mm)</th>
<th>4</th>
<th>4.2</th>
<th>4.4</th>
<th>4.6</th>
<th>4.8</th>
<th>5</th>
<th>5.2</th>
<th>5.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>pressure</td>
<td></td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>15</td>
<td>13</td>
</tr>
</tbody>
</table>

In Table A-2 the C'' of the sample is given at different voltage levels. As explained before the sudden change in C'' indicates a PD inception, and here this occurs at 5.2 kV/mm.
Table A-3: C" at different voltages at 220 mbar and 1.8 mbar pressure

<table>
<thead>
<tr>
<th>Voltage (kV/mm)</th>
<th>1.4</th>
<th>1.6</th>
<th>1.8</th>
<th>2</th>
<th>2.2</th>
<th>2.4</th>
<th>2.6</th>
<th>2.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>220 mbar pressure</td>
<td>2.42E-14</td>
<td>2.42E-14</td>
<td>2.457E-14</td>
<td>2.519E-14</td>
<td>2.493E-14</td>
<td>2.518E-14</td>
<td>3.832E-13</td>
<td>9.420E-13</td>
</tr>
</tbody>
</table>

In the test run at 220 mbar, it is observed from Table A-3 that the PD inception voltage is lower at 2.6 kV/mm; it indicates that the PD inception voltage was affected by the change in pressure. At even lower pressure at 1.8 mbar PD is already starting at 1.8 kV/mm.

From Table A-2 and Table A-3 it is understood with the low pressure the PD inception voltage decreases, but according to the Paschen curve the breakdown voltage should be increasing at this level of pressure and with a gap of approximately .01 mm between the sample and electrodes. What actually happens was understood when the glowing spark was seen through the window of the test cell, actually the PD was occurring within the whole test cell at very low pressure, because the low pressure decreases the breakdown strength of air, the gap between the electrode and the metal test cell multiplied by the pressure was still on the right side of the Paschen curve minimum even though for the small gap between the test object and electrode the Paschen minimum was crossed.

After observing this phenomenon it was concluded that going to low pressure in a test cell would not help to achieve higher PD inception voltage.
Appendix B

Thickness Experiment Data

Thickness and diameter evolution of samples at 22 °C

![Graph showing thickness change of samples at 22 °C](image)

Figure B.1: Thickness change of samples at 22 °C

![Graph showing diameter change of samples at 22 °C](image)

Figure B.2: Diameter change of samples at 22 °C
Thickness and diameter evolution of samples at 35 °C

Figure B.3: Thickness change of samples at 35 °C

Figure B.4: Diameter change of samples at 35 °C
Thickness and diameter evolution of samples at 50 °C

Figure B.5: Thickness change of samples at 50 °C

Figure B.6: Diameter change of samples at 50 °C
Thickness and diameter evolution of samples at 65 °C

Figure B.7: Thickness change of samples at 65 °C

Figure B.8: Diameter change of samples at 65 °C
Thickness and diameter evolution of samples at 70 °C

Figure B.9: Thickness change of samples at 70 °C

Figure B.10: Diameter change of samples at 70 °C
Appendix C

Temperature log of HV laboratory

Another very important issue affecting the dielectric measurements that had to be considered is the temperature during dielectric measurements. It is known in the literatures that the dielectric measurements are affected by the temperature [50]. Thus it had to be made sure that the temperature during all measurements was the same for comparing the results. The temperature in the high voltage lab was known to be around 22 °C but to make sure it remains the same at night. The temperature was logged in the computer using a thermocouple and electrometer setup. The following graph shows the temperature variation in the lab over 20 h. The values were very consistent over the time period which confirms the fact that all measurements were conducted in the same temperature.

Figure C.1: Temperature profile in high voltage laboratory